MSEL PROGRAMMATIC/TECHNICAL ACCOMPLISHMENTS

This section contains selected highlights of MSEL research for the last 12 months. The highlights are arranged by programs within the four major program groups: Materials Characterization, Measurement Facilities, Materials Manufacturing, and Functional Materials. Significant advances were achieved in combinatorial methods, materials for microelectronics and wireless communications, x-ray characterization, modeling and metals processing.

MATERIALS CHARACTERIZATION

Combinatorial Methods

Combinatorial Characterization of Polymeric Thin Films and Coatings (May 2000)

Recently, Carson Meredith, Alamgir Karim, and Eric Amis of MSEL's Polymers Division have developed methods for rapid measurements of the properties of polymer coatings. Polymeric coatings play an important role in many industrial applications, such as automotive, electrical, and aerospace industries where their stability and integrity is of fundamental importance. The NIST researchers adapted the concept of combinatorial and high-throughput analysis for rapid acquisition of properties data on polymer coatings that would be useful in fundamental studies, validation of physical models, or exploration of industrial applications. Combinatorial methods of drug discovery in pharmaceuticals research are well known, and more recent applications of the methodology have led to the discovery and synthesis of new inorganic materials, catalysts, and organic polymers.

The material properties of polymeric coatings are sensitive to a variety of factors, including composition, temperature, and thickness. Most polymeric coatings are also multicomponent blend materials and the miscibility of the blend components is an important issue that affects ultimate properties. To acquire data covering a range of variables is both time consuming and expensive when done by traditional methods. The novel approach developed included methods for depositing polymeric coating libraries that employ continuous gradients in thickness, composition, and temperature. Each "library," which is the size of a standard microscope slide, contains as many as 1,500 differentiable conditions such as film thickness, composition, and temperature. Analysis of these libraries provides characterization of fundamental properties and thin-film phenomena occurring in such coatings. By automating ellipsometry and optical microscopy for high-throughput screening, the dewetting and polymer blend phase separation behavior were characterized in orders of magnitude less time than with conventional methods. The high-throughput techniques produce a large amount of data over a broad range of parameter values, so that novel regimes of kinetic and thermodynamic behavior can be observed.

NIST Database on Composite Reinforcements Now Available on WWW (November 1999)

A NIST database for composite reinforcements is now available on the World Wide Web. A critical manufacturing variable of reinforcements used in structural composites is their permeability, which is the ability of polymeric resins to flow through their porous structures. The database was developed jointly with the TS Standard Reference Data Program and MSEL's Polymers Division to report permeability data from NIST measurements. Companies in the automotive and other industries have been purchasing the database since it was released in 1998 in disk format and they use the data in process design activities. The availability of the database on the World Wide Web will improve industry access as well as provide the opportunity for expansion through additional data from external laboratories.

Advances in Process Visualization Reveals Novel Polymer Structure (January 2001)

Scientists from MSEL's Polymers Division have utilized in-situ visualization technology to discover novel structures formed during processing of polymer blends. The observations, which will appear in Physical Review Letters, are the consequence of new measurement tools developed for elucidating the structure of polymer blends during processing. The novel structure results when the dimension of a manufactured part approaches the size of one of the components in an incompatible mixture of polymers. Under such conditions, the NIST measurements show that there is a massive reorganization of the structure of the dispersed polymer droplets. In a four-stage process, tens of thousands of the droplets join together to form extremely large strings. Instead of micrometer-sized droplets typical of polymer blending, these strings can be 10 centimeters in length, and have been observed to wrap around the processing flow. Once the strings form, they are extremely stable; in fact, it is hard to get rid of them.

Most engineering plastics are polymer blends. Polymer blending technologies are well developed for the case where the final part, such as a car bumper, is much larger than the size of the dispersed polymer droplet, typically one micrometer. The new observations suggest the need for alternative blending strategies when the size of the part becomes comparable to the size of the droplets. In addition, the string-like structure may lead to new applications, for example, conductive plastic wires, if the string component was a conductive polymer and the matrix was an insulator with good mechanical properties. If the string component formed a reinforcing fiber, one could have ultra-thin composite materials of high one-dimensional strength. Likewise dissolving out the string component from a biocompatible polymer could provide oriented pores for cell growth for tissue engineering.

Polymeric Characterization

International Interlaboratory Testing Advances Mass Distribution Measurement Method for Synthetic Polymers (October 2000)

The quality of mass spectrometric measurements of mass distribution in synthetic polymers was assessed in a recent NIST report that described the results of an international interlaboratory comparison involving 21 laboratories, including MSEL's Polymers Division. MALDI-MS, a form of mass spectrometry in which laser ablation is used to produce volatile charged molecules, is being explored as an absolute method for molecular mass distribution of synthetic polymers. Most current methods yield only moments of the mass distribution. For instance, gel permeation chromatography yields the mass distribution but requires calibration with hard-to-find standards of known mass.
Published results of mass distribution by mass spectrometry yield conflicting findings; hence the interlaboratory comparison was undertaken to determine the current status of measurements on a single, well-characterized polymer and to identify measurement issues that require attention. The polymer, polystyrene, evaluated in the round robin was custom synthesized to NIST specifications with molecular characteristics such that it could be investigated not only by mass spectrometry but also by traditional spectroscopic methods and light scattering.

Participants of the interlaboratory comparison reported the mass spectrum of the polystyrene and moments of the distribution calculated from mass spectrometric data. NIST staff calculated the moments from the submitted data as well. In some cases, the moments calculated by NIST using the participants' data differed significantly from moments reported by the participants. The distribution in values of moments calculated by NIST was very narrow, with a standard deviation of one polystyrene repeat unit, approximately. Furthermore, analysis of these data yielded moments of the mass distribution lower than those obtained from current methods but within the measurement uncertainty. Nonetheless, it was found that calibration of mass spectrometers was not performed correctly by several participants and that methods of data analysis differed widely with some participants reporting moments of the distribution that differed significantly from the mean. The findings of the report will be used to improve the quantification of the new mass spectrometric method for the determination of synthetic polymer mass distributions.

Ultrasonic Characterization of Materials

New Method for Measuring the Internal Friction in Solids (January 2000)

Internal friction describes the mechanisms of dissipation of mechanical energy inside a solid. It is an important physical property needed for materials characterization because it often exposes atomic level phenomena that control such important physical properties as mechanical strength, hardness, and atomic diffusion. In order to measure it, all other sources of energy loss must be eliminated by careful control of the experimental conditions. This seldom can be achieved outside a laboratory environment so its application to non-destructive evaluation of a structure or a device is limited severely. MSEL's Materials Reliability Division recently has performed research on a technique called "diffuse field ultrasonics" in which ultrasonic waves in the 0.1 to 10 MHz frequency range are allowed to diffuse throughout a solid body of arbitrary shape while their decay in amplitude is monitored as a function of time. The results obtained on acommercial aluminum alloy show that the intrinsic internal friction observed in this way is comparable to that observed by non-contacting methods which minimize the effects of contacting transducers. In addition, results on steel alloys used in nuclear reactor pressure vessels show a systematic relationship between the internal friction and the hardness. These results represent a significant step towards utilizing the diffuse field technique for nondestructive evaluation of in-service structures as well as for elucidating the relationship between internal friction and hardness.

MSEL Measures the Elastic Properties of Thin Films with Ultrasound (September 2000)

Surface coatings are used throughout industry to give ordinary materials extraordinary resistance to wear and corrosion as well as to provide specialized electrical or magnetic properties for device applications. Knowledge of the elastic properties of the coating is important not only for estimating the residual thermal stresses but also for ensuring that the desired microstructure is present. During the past two years, an ultrasonic technique has been developed in which lasers are used to launch and detect surface waves that propagate along the coated surface of a thick substrate. Because the transducers use optical interactions with the substrate and the film, they are non-contacting in nature and can operate at frequencies extending up to hundreds of megahertz. This allows the surface wave velocity to be measured with high accuracy at wavelengths extending down to tens of microns. Theoretical models that relate the elastic constants of the film and substrate to the surface wave velocity are available in the seismology and surface acoustic wave device literature but they are cumbersome for deducing the film properties from measurements of the surface wave velocity.

The program at MSEL's Materials Reliability Division in Boulder has advanced the technology both experimentally and theoretically by dealing with elastically anisotropic materials at frequencies approaching 500 MHz and by developing a Green's function formalism that speeds up and simplifies the deduction of elastic properties from surface wave velocity measurements. These new capabilities recently have been used in a cooperative program with CSIRO in Australia to measure the elastic properties of a series of submicron thick TiN films deposited on silicon single crystal wafers. These films were of particular interest because they were elastically anisotropic and supported a range of residual stresses.

Nondestructive Testing of Cables (December 2000)

Cables formed by twisting steel wires together to form a flexible rope with high-strength properties are found throughout industry. However, the nondestructive detection of internal flaws such as cracks or corrosion in the innermost wires is very difficult for conventional nondestructive testing techniques because of the naturally inhomogeneous nature of the cable's construction. Recently, the Colorado School of Mines and MSEL's Materials Reliability Division in Boulder collaborated on the development of a novel method of inspection of copper cables used for grounding power transformers in electrical substations. Here, the cables run underground with the only access being a short length between the transformer frame and the surface of the ground. A special ultrasonic transducer was designed that could be clamped around the exposed end of the cable. The transducer sends a torsional ultrasonic wave along the cable buried under the substation. By detecting and signal processing the echo signals returned by corroded regions, the damage can not only be located but its severity can be estimated. This inspection technique is now being applied to high-voltage transmission line cables made of steel and aluminum wires twisted together to optimize the conductivity-to-strength ratio. The work at the Colorado School of Mines is supported by a contract with EPRI.

MEASUREMENT FACILITIES

Neutron Characterization

Unraveling the Puzzle of Molecular Sieve CIT-1 (October 1999)

Zeolitic molecular sieves are made mostly of silicon and oxygen and have tiny, precise holes that will only fit some molecules, so for example, gasoline can fit inside, but not crude oil. They are used commercially to make gasoline, separate air into oxygen and nitrogen, capture radioactive ions; they can be found between the panes of double-pane windows and are even put in laundry detergents to soften water. Making these molecular sieve materials is as much an art as a science because so little is understood about how these materials form. One important question is why two reasonably different trimethylammonium cations will coax silicon, oxygen, and other atoms into exactly the right positions to make the molecular sieve CIT-1. In one cation, the ammonium group is attached to a tricyclodecane ring and in the other cation, the ammonium group is attached to a myrtanyl ring. However, moving the ammonium group over by carbon atom along the myrtanyl ring makes a cation that cannot be used to make a molecular sieve in the CIT-1 family. Researchers at NIST, along with collaborators from the California Institute of Technology and the State University of New York, Stony Brook, studied the CIT-1 zeolite, while the holes were plugged with ammonium cations. They used neutron and synchrotron diffraction as well as computer modeling and found that the shape of the cations that make CIT-1 were matched perfectly to the holes. However, when the researchers moved the ammonium group one position, the subtle shape change was just enough to keep the cations from fitting. This kind of information will help other researchers find new ways to make molecular sieves.

NCNR Confirms Silicone-Filler Model and Achieves a Measure Beyond (October 1999)

MSEL Polymers Division researchers, in collaboration with Dow Corning Corp., have completed a study of filled polymers using small-angle neutron scattering (SANS) instrumentation at the NIST Center for Neutron Research. The measurements probed the influence of fillers on the silicone polymer chain dimensions as a function of filler concentration and polymer molecular mass. Silicone polymers blended with particulate fillers are used commercially in rubber products and sealants. The interactions between the fillers and the polymers are key factors that influence product performance. Molecular simulations have predicted that polymer chain dimension in the presence of fillers is a function of the filler particle size and concentration. However, tests of these predictions have not been available.

The SANS measurements, on materials supplied by Dow Corning, showed that polymer chains which are approximately the same size as the filler particle in the unfilled material experience a decrease in chain dimensions at all filler concentrations. In contrast, for larger chains, at low filler concentrations, an increase in chain dimensions relative to the unfilled chain dimensions is observed. Both results are in agreement with existing predictions from molecular simulations.

However, at even higher filler contents, which are beyond the scope of the molecular simulations, the chain dimensions reach a maximum value before decreasing to values that are still larger than the unfilled chain dimensions. A qualitative excluded-volume model was proposed to account for the experimental results. The extension of the experimental data beyond the existing calculations provides researchers with the necessary data to supplement current predictions. Furthermore, the measurements suggest that changes in chain dimensions in filled polymers should be considered when predicting their mechanical performance.

Neutron Studies of Novel Ferroelectric Materials Shed Light on Origin of Remarkable Piezoelectric Properties (March 2000)

Piezoelectric materials expand in the presence of an electric field. Conversely they generate an electric field when compressed. This property forms the basis of operation in solid state transducers that convert mechanical energy into electrical energy, and vice-versa. The present day material of choice for the fabrication of high-performance electromechanical actuators is the ceramic Pb(Zr1-xTix)O3 (PZT).

Recently scientists at the NIST Center for Neutron Research (NCNR) and Penn State University have developed a program to study single crystals of the ferro-electric relaxor-based materials Pb(Zn1/3Nb2/3)1-xTixO3 (PZN-xPT) and PMN-xPT (M=Mg) that exhibit remarkably large piezoelectric coefficients (> 2500 pC/N). Strain levels as high as 1.7 percent have been achieved, with little dielectric loss, that are an order of magnitude larger than those presently achievable with PZT. Such exceptional piezoelectric properties make these materials leading candidates in the next generation of solid state transducers that are crucial for industrial and defense applications.

Neutron scattering measurements at the NCNR have revealed information about the nature of the atomic vibrations in these novel materials that are related to their unusual piezoelectric properties. In particular, a key vibrational mode is found to be largely inhibited due to an underlying structure of nanometer-sized polarized domains, unlike in normal ferroelectric materials. Future neutron measurements are planned to probe these vibrations in the presence of an applied electric field to further elucidate the microscopic origin of these enhanced piezoelectric properties.

Crosslinked Micellar Gel for Environmental Cleanup (April 2000)

Surfactants are commonly used in detergency applications where several hundred surfactant molecules aggregate to form a micelle consisting of a hydrophobic core that is shielded from its aqueous environment. Unwanted (often oily) solutes are spontaneously solubilized in the hydrophobic cores of the micelles, providing a homogeneous dispersion of oil in water where the oil is effectively concentrated inside the micelle. Unfortunately, the oil-containing micelles are typically too small (ca. 5 nm) to be removed from the water by conventional methods such as filtration or centrifugation. Stabilized "macro-micelles" would provide a method for not only concentrating contaminants, but also removing them from solution.

Recently, Steve Kline, a chemical engineer and instrument scientist in the NIST Center for Neutron Research (NCNR), succeeded in synthesizing a surfactant-based material that retains features and functionality of surfactant micelles and benefits from the structural stability of a crosslinked polymer matrix. The material, a crosslinked micellar gel, is prepared by a simple one-step aqueous polymerization of the surfactant cetyltrimethylammonium 4-vinylbenzoate to which a small quantity of a crosslinker, divinyl benzene, has been added. As prepared, the gel is only 1 percent surfactant and 99 percent water by mass but can easily be handled and cut to a desired shape.

Physical characterization of the micellar gel at the NCNR by small-angle neutron scattering has confirmed that the structure of the gel is that of cylindrical micelles between crosslinks. The micelles have a circular cross-section of 4 nm, and an average pore size of 40 nm. The pore size is adjustable by controlling the initial surfactant concentration. The micellar gel is capable of solubilizing common hydrocarbons and other hydrophobic solutes. The most significant advantage of the micellar gel is that once oily material has been solubilized and concentrated in the gel, the gel (and the contaminant) can simply be lifted from the solution. This material clearly has promise in use for wastewater cleanup (gasoline, for example). Other possible applications include a controlled release matrix for drug delivery, a porous matrix for gel electrophoresis, or a selective filter membrane. A patent is pending on the material and work is continuing toward defining a class of crosslinkable micellar materials.

The Measurement of Elastic Properties of Sprayed Coatings by Neutron Diffraction (June 2000)

Thermal sprayed coatings play an important role as protection against thermal and corrosive exposure, wear and mechanical loads. Due to the defect structure and porosity of thermally sprayed deposits, their elastic constants become anisotropic and they can differ significantly from those of bulk materials with the same chemical composition. The knowledge of the elastic properties can be essential for the analysis of stress/strain behavior critical for performance and lifetime assessments.

Very recently, MSEL researchers introduced a new method for measuring these elastic constants by means of diffraction. Experimentally, the method relies on lattice strain measurements under applied load for various specimen directions and crystallographic reflections (hkl). By means of neutron diffraction it was possible to measure the elastic behavior perpendicular and parallel to the surface of thin coatings in an in-situ load device, thus making a full set of elastic data for the two principal coating directions available. Using the recently developed theoretical relationship between these experimental data and the coating elastic constants, the latter quantities can be calculated, thus making important engineering data accessible by means of a new and relatively simple method.

Quasielastic Neutron Scattering Probes Protein Dynamics (October 2000)

The function of a protein depends critically on its ability to adopt a specific structure. Remarkably a protein can fold efficiently to this native state from the unfolded states on physiological time scales. Understanding how this process occurs is one of the great challenges in biology. Proteins can also form collapsed, partially folded states. Such partially folded proteins resemble the intermediate states along the protein folding pathway and play important roles in understanding the mechanisms of protein folding.

To understand the changes in protein dynamics that occur in the final stages of folding, scientists from the NCNR and MSEL's Polymers Division have used quasielastic neutron scattering to probe the differences in the dynamics between the native state and the almost completely folded, molten globule state of the protein bovine a-lactalbumin. The results, show that the side-chain protons in the molten globules are significantly more mobile than those in the native protein. Moreover, the length scale of the motion, information that is uniquely provided by neutron spectroscopic techniques, is substantially longer in the molten globule state compared to that in the more compact native state.

Supercooling and Superheating of Vortex Matter (January 2001)

The behavior of quantized flux lines in type-II superconductors is of critical importance in a variety of high-current applications anticipated for “high temperature” superconductors, such as magnets for medical imaging and power transmission cables. These vortex systems also provide a prototypical system for the study of fundamental problems in phase transitions and melting phenomena. Unfortunately, vortex structures have been difficult to investigate in detail in the cuprate materials because of the intrinsically short superconducting length scales and because of materials quality problems. A current subject of wide interest concerns the possibility of a solid-liquid transition of vortex matter and its relation to the dramatic transport anomaly in superconductors known as the peak effect, in which the critical current exhibits a maximum rather than decreasing monotonically with increasing temperature. Researchers at Brown University and the NCNR have now carried outsmall angle neutron scattering measurements combined with in-situ ac magnetic measurements, on a high-quality niobium crystal where these experimental difficulties are averted. They report the first structural evidence for a first-order vortex solid-liquid transition associated with the peak effect. In particular, superheating of the vortex solid and supercooling of the vortex liquid have been observed directly for the first time. This is an important result for assessing future technological applications, since there is a definite limit, by virtue of being a first-order transition, to which the material's properties can be tailored to achieve the highest critical currents. These results also open up the possibility to experimentally test the fundamental theoretical ideas of melting in bulk solids. For example, in conventional solids surface melting masks any superheating effects, while a superheated vortex lattice is stable for hours, but can be melted by applying a small perturbing ac magnetic field.

Neutron Facility Operation

Polymer Chain Motion (November 1999)

The first experiments on the nation's only neutron spin echo (NSE) spectrometer recently have been performed at the NIST Center for Neutron Research (NCNR). This cold neutron spectrometer allows measurements of key dynamic process in macromolecular systems essential to researchers in polymer, biomedical, and colloid science. The instrument covers a combination of time- (0.01-100 ns) and length-scales (0.2-20 nm) previously inaccessible in the United States. Unique measurements of slow dynamics in other areas of materials and chemical engineering—including, for example, giant magnetoresistance materials and supercritical fluids—are also expected. The measurement of dynamic processes out to 100 ns is 1000 times longer than previous U.S. capabilities.

This new instrument was developed in partnership with Exxon Research and Engineering and the Forschungszentrum Juelich in Germany. Work on the spin echo is expected to allow more realistic models of why and how molecules move. Thus scientists will be able to better predict and improve macromolecular properties. A general call for experiment proposals from the research community will be issued at the end of 1999.

FANS-I Commissioned at the NCNR, with 20 Times the Intensity of Inelastic Neutron Scattering (May 2000)

The increasing complexity of new materials and processes is an important factor driving the development of new characterization tools. The traditional vibrational spectroscopies, infrared absorption and Raman scattering, have long played a central role. Neutrons are a more versatile dynamical probe than photons, but inelastic neutron scattering long has suffered from the comparatively low intensity. To address this, a new, high-intensity filter- analyzer neutron spectrometer (FANS) is being constructed in two phases at the NIST Center for Neutron Research by a consortium of scientists from the University of Pennsylvania, the University of California at Santa Barbara, NIST, Hughes Aircraft, and DuPont. The first phase of FANS recently has been commissioned. The measured intensity exceeds that of the previous instrument by a factor of ~20, providing significant new measurement opportunities for the U.S. scientific community. For instance, FANS will be used to study intra- and intermolecular vibrations in molecular crystals; polymers; and guest-host systems including hydrogen in metals, hydrocarbons in zeolite catalysts, sorbed gases on surfaces and clathrates for fine chemical separation. It also will be used to characterize novel forms of carbon including fullerenes, nanotubes, foams and aerogels, amorphous carbons, and fibers as well as environmentally acceptable refrigerants, gas separation materials, and the hydration reaction of cements.

New Neutron Spectrometer Commissioned at NCNR (August 2000)

The first guest experiment, by Zimei Bu (Penn State University and MSEL's Polymers Division) and co-workers, studying the molecular dynamics of alpha-lactalbumin, has recently been performed on the disk chopper time-of-flight spectrometer (DCS) at the NIST Center for Neutron Research (NCNR). This instrument, which provides U.S. researchers access to world-class capabilities in the vital area of cold neutron spectroscopy, allows scientists to study dynamical processes in materials on time scales of less than 100 ps. As such it complements the neutron spin echo and backscattering spectrometers at the NCNR, which probe longer time scales, and the recently commissioned FANS spectrometer, which probes shorter ones. During the commissioning phase the DCS, the world's most flexible instrument of its type, has demonstrated state-of-the-art sensitivity. This combination allows researchers unprecedented ability to tailor the instrumental conditions to the physical processes of interest. Thus, the DCS is a unique tool, allowing measurements in important areas of research such as bio-processes, energy storage, glassy dynamics, chemical separation, and catalysis.

NCNR Puts into Operation New Perfect NCNR Crystal Diffractometer for Ultra-High Resolution SANS (September 2000)

A perfect crystal diffractometer (PCD) for ultra-high resolution small-angle neutron scattering (USANS) measurements is now operational at NIST's Center for Neutron Research (NCNR). The PCD increases the maximum size of features accessible with the NCNR's 30-m long, pinhole collimation SANS instruments by nearly two orders of magnitude, from ~ 102 nm to 104 nm.

The PCD is a Bonse-Hart-type instrument with large triple-bounce, channel-cut silicon (220) crystals as monochromator and analyzer. The perfect crystals provide high angular resolution while the multiple reflections suppress the "wings" of the beam profile, improving the signal-to-noise ratio to values comparable to that obtained with pinhole instruments. This technique, widely utilized for X-rays for many years, only recently has been adapted successfully for neutrons, as dynamical diffraction effects arising from the deep penetration of neutrons in thick perfect crystals have become understood. The design of the NCNR's PCD successfully eliminates these undesirable effects, resulting in a signal-to-noise ratio of 105 at a minimum scattering vector Q = 0.0004 nm-1. The performance of the NIST instrument is either superior or comparable to that of any USANS instrument currently in operation worldwide.

The measurement range of the PCD overlaps that of the NCNR's 30-m SANS instruments. Together they probe structure in materials over four orders of magnitude, from ~1 nm to 104 nm. Combined measurements on these instruments will enable hierarchical and highly anisotropic microstructures in materials, for example, in fiber or clay impregnated nanocomposites, to be more fully characterized. The PCD is part of the NIST/NSF Center for High Resolution Neutron Scattering (CHRNS) with up to two-thirds of the available beam time to be allocated by the NCNR's Program Advisory Committee to scientists and engineers who submit proposals for peer review.

NCNR Sets the Standard for Quantitative Phase Analysis (December 2000)

Personnel from the NIST Center for Neutron Research (NCNR) recently participated in an international round-robin on the use of diffraction techniques for the quantification of phase abundance in multiphase mixtures. This type of analysis is essential for the characterization, development, and performance of many industrial materials, such as thermal barrier coatings employed in aircraft engines. The round-robin included participants from X-ray, synchrotron, and neutron facilities worldwide, and was sponsored by the Commission on Powder Diffraction of the International Union of Crystallography.

Results to date show a wide variation in performance for various methods. For example, in one standard mixture containing 34.2 percent zinc oxide, results obtained using laboratory X-ray sources ranged from 25 percent to 42 percent, results from synchrotron sources ranged from 29 percent to 35 percent, and those from neutron sources ranged from 32 percent to 35 percent. NCNR analysis gave 34.4(1) percent. For all 10 mixtures analyzed, the NCNR results agreed within statistical limits with the nominal compositions and, overall, gave the best results in the study.

The results of this study again emphasize the importance of neutron methods in providing accurate data on phase composition in industrial materials.

X-Ray Characterization

MSEL Ceramics Division Commissions New X-Ray Instrument at Advanced Photon Source for Characterization of Anisotropic Materials (March 2000)

As part of a collaboration, known as UNICAT, with the University of Illinois, Oak Ridge National Laboratory, and UOP Research, researchers in MSEL's Ceramics Division have developed novel small-angle X-ray scattering (SAXS) methods at the Advanced Photon Source (APS) to characterize anisotropic alloy and ceramic microstructures such as found in coatings, laminates and highly textured materials. While pinhole-geometry SAXS and SANS instruments, with their two-dimensional detectors, can characterize anisotropic microstructures in the nanometer to 0.1 micrometer scale regime, this range is not easily extended to larger sizes unless multiple scattering methods are used. Double-crystal Bonse-Hart ultrasmall-angle X-ray scattering (USAXS) instruments can extend the scale regime to several micrometers, but the data are intrinsically slit-smeared, and the standard USAXS configuration is not suitable for anisotropic studies.

To remove this limitation, transverse crystal reflections orthogonal to the plane of the main USAXS monochromator/collimator and analyzer crystal reflections were introduced. While the data in a single scan are still associated with one azimuthal direction in the plane of the sample, the transverse crystal reflections remove the slit-smearing and effectively restore a pinhole geometry. To study an anisotropic microstructure, the sample must be measured repeatedly for different azimuthal orientations with respect to the incident beam. However, this is not a disadvantage for highly anisotropic microstructures because the resolution of the azimuthal rotation increments can be made almost vanishingly fine. Indeed, the anisotropic resolution of the new instrument can surpass that of conventional SAXS or SANS instruments with a two-dimensional detector.

The anisotropic USAXS configuration also takes advantage of innovations previously introduced into MSEL's standard USAXS design, including a continuously tunable X-ray wavelength, and a photodiode detector with a 10-decade linear dynamic range that enables a primary absolute intensity calibration to be made with respect to the incident beam. Early anisotropic studies have focused on the microstructural characterization of plasma-sprayed coatings and of cracking in highly textured brittle ceramics. However, it is envisaged that the anisotropic USAXS capability could open up a potentially wide field of quantitative microstructure characterization in thin films and coatings on substrates, using a glancing-angle reflection geometry.

MSEL Collaboration Uses Microgravity to Improve Protein Crystal Growth (November 2000)

NIST scientists are collaborating with Biospace International in the growth of ribonuclease crystals in space. X-ray diffraction topography, which has only recently been applied to protein crystals, was used to probe the differences between crystals grown on the space shuttle and crystals grown at the same time on the earth. The topographs from the space-grown crystals showed that they were of higher crystalline perfection than the ground-grown crystals. The images of the space-grown crystals were more uniform and sharply defined. The symmetry was consistent with nucleation followed by homogeneous symmetric growth. This growth mechanism is possible in microgravity but not likely on earth where there is sedimentation and convection-induced asymmetry. On the other hand, the earth-grown crystals had a less well-defined microstructure with no clearly identifiable features and there was no consistent symmetry of the images. All of these features indicate lower quality crystals with a higher-defect density. In addition to quality improvements, microgravity also improves crystal harvesting. Approximately 80 percent of the crystals grown in microgravity were free-floating in the growth chamber, facilitating removal. In contrast, approximately 80 percent of the earth-grown crystals grew attached to the growth chamber making harvesting more difficult. These results clearly demonstrate the advantages of a microgravity environment for growing protein crystals.

New X-ray Imaging Technique Reveals Crystal Defects (December 2000)

The deformation of metals takes place primarily by the motion and interaction of defects in the crystal structure known as dislocations. Quantitative understanding of this deformation, needed for modeling of metal-forming processes, has been hampered by a lack of knowledge about the complex configurations assumed by these defect microstructures when the metals are deformed.

A new experimental technique, ultra small angle X-ray scattering (USAXS) imaging, has been shown jointly by the Metallurgy and Ceramics Divisions of MSEL to hold promise as a useful tool for studying microstructures in situ. The technique is based on forming an image of the sample using X-rays which have been scattered from defects in the crystal structure. Although these X-rays scattered from defects are very weak, the USAXS technique allows them to be isolated from the high-intensity background to form an image of the defects only. The scattering from these components can be detected down to around seven to ten times the intensity of the main transmitted X-ray beam. Preliminary tests of this technique were made at the Advanced Photon Source on March 11-13, 2000, using copper samples in which defects had been produced by a very slow deformation treatment. A more thorough study was conducted on May 17-21, 2000. The tests were very successful and microscopic damage was imaged using several different scattering conditions. A basic theory for the image formation process in USAXS imaging has been worked out and it was validated by experiments completed on Sept. 4, 2000. The technique is believed to be a major breakthrough with broad potential applications, including the study of the defects which control metal deformation behavior. A paper on USAXS imaging has been accepted for publication.

MATERIALS MANUFACTURING

Ceramic Coatings

New Method for Materials Measurements at Very High Temperatures (July 2000)

A significant number of refractory inorganic and ceramic materials undergo melting and vaporization transformations at very high temperatures, particularly over the range of 2,500 K to 5,000 K. However, virtually no direct thermochemical data are available for this range as conventional measurement methods are limited to temperatures below about 2,500 K. Researchers in MSEL's Ceramics Division have developed new measurement methods for determination of temperature, pressure, and vapor phase molecular composition at thermal equilibrium for this elevated temperature range. The methods utilize pulsed laser heating with in situ mass spectrometric and optical spectroscopic monitoring of pressure and temperature transients. Results have been obtained for the ZrO2-Y2O3 system, for which partial pressure data are needed by the aerospace industry for thermal spray and electron beam processing of thermal barrier coatings. Related results obtained for other refractory materials such as C, Al2O3, and SiC have been used to test the reliability of the critical evaluation and extrapolation procedures used to generate the widely used NIST-JANAF thermochemical tables. With this direct measurement approach, improvements in data reliability by an order of magnitude, or more, are found. Initial results of this work recently were presented at the 10th IUPAC Conference on High Temperature Materials Chemistry, April 10-14, 2000, Julich, Germany, and at a NIST workshop, May 14, 2000, on non-contact thermometry.

Ceramic Manufacturing

International Round Robin Testing Completed on Ceramic Powders (November 1999)

MSEL's Ceramics Division completed an international round robin study on properties of advanced ceramic powders. Thirty-four laboratories participated, including Belgium, Germany, Japan, Sweden and the U.S. The ultimate goal of this activity, conducted under the auspices of the International Energy Agency (IEA), is to draft uniform standard test methods in each participating country and through the ISO. The properties measured included those used for characterization of powders suspended in water (particle dispersion and rheology), characterization of spray dried powders (flow rate, particle size distribution, moisture and binder content), and green body evaluation (bulk density and green strength). The compiled data were analyzed to determine the repeatability of the data within each laboratory and to examine variations in the data obtained by different laboratories. In general, no significant variations occurred within the laboratories. However, significant variations between laboratories were observed for a few measurement procedures, even though the procedures had been predefined. The measurement procedures that resulted in unacceptable variation will need further evaluation and improvement before establishing national and international standard test methods for characterization of ceramic powders.

Reference Material 8983 Completed for Nitrogen, Oxygen and Carbon in Silicon Nitride Powder (February 2000)

A new Reference Material intended primarily for use as an analytical standard for the determination of nitrogen, oxygen, and carbon in silicon nitride powders has been completed. Silicon nitride is a widely used high-temperature ceramic for industrial applications requiring high fracture and wear resistance and is manufactured by compaction and sintering of powders. Any chemical impurities present in the starting powders will adversely affect the final properties of the material. Therefore, both metallic and non-metallic impurities such as nitrogen, oxygen, and carbon in the powder must be controlled to within certain limits.

A review of analytical methods used in the determination of these three elements was conducted and the high-temperature combustion method based on the ASTM E 1019 test method was selected for analysis and certification. However, it was necessary to modify the standard test method originally developed for metal powders before it could be applied to silicon nitride.

One unit of RM 8983 consists of a bottle of approximately 4.5 g of silicon nitride powder. The reference values for total nitrogen, oxygen, and carbon are 29.23+1.06, 1.20+0.14 and 0.107+0.015 mass fraction (%), respectively.

The modified tests method has been submitted to ASTM C28.05 (Advanced Ceramics) for approval as a new ASTM method dedicated to the analysis of ceramic powders. The combination of this new RM and the ASTM test method fulfill the industrial need for a calibration standard and measurement protocol for analysis of impurities in silicon nitride.

SRM 2100: First in the World for Ceramic Fracture Toughness (May 2000)

Accurate fracture toughness measurements are important for new materials development and materials specifications. Standard Reference Material (SRM) 2100 is the first reference material in the world for the property fracture toughness. This ceramic SRM, which was prepared by George Quinn of MSEL's Ceramics Division and Robert Gettings of the TS SRM office, may be used to verify fracture toughness testing procedures. It complements the new ASTM Standard Test Method C 1421-99 as well as two International Organization for Standardization (ISO) draft standards now under development. This SRM, for which the fracture toughness (Kc = 4.57 ± 0.23 Mpam) is known with a high accuracy and precision, should dramatically improve fracture toughness testing procedures for brittle materials.

SRM 2100 consists of five hot-pressed silicon nitride flexure specimens cut from a single master billet. The SRM may be used with any credible fracture toughness test method, but has been optimized for beam bending type tests. ASTM C 1421 features three such tests: the surface crack in flexure (SCF), precracked beam (PB) {also known as single-edged precracked beam (SEPB)}, and chevron notch in bending (CNB) methods. The SRM specimens are common 3 mm × 4 mm × 47 mm beams which must be precracked by the users.

Metals Processing

Model Developed for Bonding of Superalloys (November 1999)

A model has been developed in MSEL describing the process of transient liquid phase (TLP) bonding, which can be used to make high-quality joints in superalloys and other materials. An important application of this process is to make large, complex single-crystal components by joining together smaller single crystals, since defect-free small single crystals can be produced more easily than large ones. In TLP bonding, the pieces to be joined are fitted together, with a thin foil of a lower-melting alloy between them. When the assembly is heated, the foil melts but then resolidifies isothermally as its constituents diffuse into the adjoining crystal, leaving a virtually invisible joint.

The model developed in MSEL is based on a thermodynamic model of the single crystal and bonding foil materials, a matrix of diffusivities, and a reaction path model describing the diffusion process. A major consideration in the design of a TLP bonding process is the possibility that undesired crystallographic phases will form in the vicinity of the joint, causing unacceptable weakness. Use of the model enables a designer to analyze how the formation of such undesired phases will be affected by the bonding foil composition and the thermal cycle to which the assembly is exposed, and thus to design a process to avoid formation of the undesirable detrimental phase.

Application of the model has been demonstrated for a simple Ni-based alloy with a bonding foil containing boron. Application to a more complex superalloy system will require incorporation of additional thermodynamic data. With successful application of TLP, industry will be able to create stronger, more complex part geometries enabling higher efficiency engines.

Industry Funds Commercialization of NIST Modeling Technology (January 2000)

Currently, there are about 20 kilograms of powder metallurgy parts in automobiles. These are extremely cost-effective parts, and there is a great desire in the industry to increase the number of parts made by powder metallurgy. There also is an intention to switch to aluminum based powder metallurgy to reduce the weight and increase the efficiency of automobiles. For several years, MSEL's Metallurgy Division has been working with a consortium formed by the U.S. Automotive Manufacturing Partnership (USAMP, a subset of USCAR, U.S. Council for Automotive Research) to develop modeling technology that could shorten the time required to launch new powder metallurgy parts in autos and decrease their production costs. The modeling research was done as a collaborative effort between Cambridge University's Micromechanics Centre and the Materials Performance Group in MSEL. With the completion and validation of a model that accurately describes the consolidation behavior of reinforced metal powders into parts such as gears, rotors, sprockets, or connecting rods, a need arose to make this approach available in user-friendly software where the computational and scientific complexities would be transparent to the user. USAMP has recently funded a small firm in Virginia to carry out this task and the Metallurgy Division is interacting with their technical staff to assure correct implementation of the model. The software will be available to the USAMP consortium members in a few months and, if successful, to the U.S. powder metallurgy industry in a year or two.

Ferrite Standards Enter SRM Inventory (March 2000)

MSEL has completed certification of a new batch of Secondary Ferrite Standards, RM 8480 and RM 8481, and shipped them to the Standard Reference Materials Program for packaging and sale. The reference materials are intended for the calibration of instruments used to measure weld metal ferrite content in accordance with ANSI/AWS Standard A4.2 and ISO Standard 8249. These standards are designed for use in welding construction and repair applications where the ferrite content of austenitic stainless steel welds must be controlled in tight ranges. RM 8480 consists of a low range (8 specimens distributed in the range of 0 to 30 FN) and RM 8481 is the corresponding high range (8 specimens distributed in the range of 30 to 120 FN). The certification process required the development of an advanced calibration procedure and included over 25,000 individual magnetic measurements, before the data could be reduced into statistical summaries. The calibration procedure and statistical summaries are included in the RM certificates and in NIST STP 260-141 "Secondary Ferrite Reference Materials: Gage Calibration and Assignment of Values."

Thermodynamic Data Predict Conditions for Alloy Electrodeposition (April 2000)

The electrodeposition of metallic alloys has been central to the growth of the electronics and magnetic recording industries. This is largely due to the exceptional properties exhibited by electrodeposited material as well as the favorable economy of scale associated with electro-deposition processes. Most often, alloy deposition proceeds at potentials well below the reversible potentials of the alloy constituents. Composition and microstructure are generally controlled by electrolyte composition, solution hydrodynamics and electrode potential. In some cases, alloys can be formed at potentials that are positive of the reversible potential of the less noble species (underpotential deposition, UPD) due to the favorable free energy associated with alloy formation.

A technology important to electronics manufacturing in which UPD plays a vital role in determining deposit properties is the electrodeposition of gold. For gold thin film growth, electrodeposition proceeds in the UPD region of an impurity metal which promotes nucleation and grain refinement. The impurity metal is incorporated only at trace levels in the deposit. It is likely that UPD alloy deposition will be seriously examined for copper metallization for future generations of on-chip interconnects requiring copper alloys. NIST's research objective is to develop the underlying theory and metrology necessary to gain a better understanding of UPD as it relates to the bulk formation of alloys. In collaboration with Professor Charles Hussey of the University of Mississippi, MSEL researchers have examined the electrodeposition of aluminum-transition metal alloys from an aluminum chloride/1-methyl-3-ethylimidazolium chloride ambient temperature molten salt. This non-aqueous electrolyte was chosen so that surface oxides and hydrogen evolution could be avoided. Using the alloy free energy data that appear in the phase diagram literature, the researchers have accurately predicted that Cu-Al, Ni-Al, Co-Al, and Fe-Al alloys can be electrodeposited at potentials positive of the aluminum reversible potential; i.e., these alloys co-deposit by a UPD mechanism. Further, the researchers can predict the potential at which alloy deposition is initiated. The alloy free energy treatment also accurately predicts that Zn-Al and Sb-Al alloys will not form by UPD. Future work will focus on the development of electrode potential—alloy composition relationships based on alloy free energy.

Fluctuations in Thermal Spray Process Measured (May 2000)

Thermal spray is a relatively low cost, but difficult to control, process for applying protective coatings to material surfaces. These coatings are often of metals or ceramics, and are used for a variety of purposes such as thermal, wear, or corrosion protection. The use of thermal spray technology is often limited, however, by the difficulty of obtaining reproducible coating quality. NIST has therefore instituted a program to use advanced sensors to study and control the spray plume, and correlate process parameters to spray characteristics and coating properties.

Using a novel two-color imaging pyrometer developed for NIST under an SBIR award, researchers in MSEL's Metallurgy Division are obtaining time-resolved spray particle temperature and velocity data in thermal spray plumes and correlating these to the selectable process parameters of the thermal spray torch control system. Combining this with a thermodynamic model of the spray torch is providing information on strategies for independent control of particle temperatures and velocities.

Other sensors are being used to analyze time- dependent fluctuations in the thermal spray plume. Such fluctuations recently have been studied by several laboratories, but their exact origin and their possible effects on the quality of the deposits have not been determined. The NIST program is using a high-speed schlieren method to visualize the hot thermal spray plume, revealing some significant low-frequency processes in addition to the higher frequency fluctuations which other investigations have revealed.

Modeling of Structural Changes in Metals (June 2000)

Metallic materials in general are composed of tiny crystals, or "grains," which form during solidification but can change in size, shape, and orientation during subsequent processing of the metal. The grain structure of a metal contributes to important mechanical and physical properties of the material, and understanding how this grain structure develops is a critical part of understanding how the metal should be processed.

Several theories have been developed to describe the development of grain structure in metals, but until now they have had difficulty describing the complex changes in geometry which occur. A new model of the motion of grain boundaries and rotation of grains in metals during casting or other processing has now been developed by Metallurgy Division scientists working in MSEL's Center for Theoretical and Computational Materials Science. This "phase field" model, based on ideas developed to model solidification, permits evolution of interfaces to be calculated on a computationally simple fixed grid. This computational benefit is obtained by allowing the interface to have a finite width, which contrasts with previous models that attempted to explicitly track the location of a sharp interface. This model of grain boundary dynamics improves upon existing phase field models of the same phenomenon in that it has a simpler mathematical representation and allows for grain rotation. These improvements will result in more accurate simulations of the casting of polycrystalline industrial materials.

Increased Accuracy for Particle Temperature Measurement (October 2000)

Scientists in MSEL's Metallurgy Division have obtained emissivity data that make possible more accurate measurements of the temperature of rapidly moving incandescent particles in thermal spray plumes. Thermal spray is used for many purposes, including deposition coatings for protection against heat, corrosion, and wear. However, it is difficult to obtain reproducible results or to determine the best instrument settings for processing new materials. One approach sought by industry is to use instrument control based on measured temperatures and velocities of particles in the spray plume.

The only method currently available to measure the temperatures of such rapidly moving particles (hundreds of meters per second) is two-color pyrometry, which derives a temperature from measurement of the light emitted in two different bands of wavelengths. It is normally assumed, due to lack of any specific knowledge, that the emissivity of the material does not depend on wavelength, so the intensity of the light in the two wavelength bands can be calculated from a standard Planck function. MSEL researchers use a special facility, which uses electrical resistance heating to heat wires and holds the wires at an elevated temperature during optical measurements. The researchers were able to make specific measurements of the wavelength dependence of emissivity of tungsten and molybdenum at temperatures up to those materials' melting points. The measurements allowed MSEL to derive a correction factor for the two-color pyrometry of these materials, which was several hundred degrees at the melting point of tungsten. Additional factors, such as oxidation, which can affect the accuracy of two-color pyrometry, will be the subject of future investigations.

FUNCTIONAL MATERIALS

Dental and Medical Materials

Molecular Orientation Found to Affect Wear in Artificial Joints (October 1999)

Ultrahigh molecular weight polyethylene (UHMWPE) is the material of choice for artificial joint replacement in orthopedic practice. Cobalt and chromium alloy is commonly used as the counterface against the UHMWPE. This material pair is currently used for hip and knee replacements and has proven to be durable and biocompatible. In the search for improved biomaterials, NIST and four companies (Biomet, Inc., Zimmer, Inc., Johnson & Johnson Professional, Inc., and Stryker Howmedica Osteonics Corp.) have teamed together to conduct research on understanding the wear mechanisms of these materials.

UHMWPE used in joints has an average molecular weight of 4 million to 6 million with 40 to 60 crystalline phase. Cross-linking of this material has produced extremely low wear. The mechanism of why cross-linking reduces wear is not understood. Using the Brookhaven Synchrotron ultrasoft beam line, scientists in MSEL's Ceramics Division have been able to measure quantitatively the degree of molecular orientation of UHMWPE as a function of rubbing direction and cycles.

Results suggest that the polymer is easily oriented by shear at the surface layer. If the motion is unidirectional, all the chains would align along the direction of motion, producing a semi-glassy solid which is prone to fracture. By cross-linking the amorphous region of the polymer, the molecular orientation from rubbing is reduced severely, producing much better wear resistance.

Silver-Based Substitute for Mercury-Containing Dental Alloys (October 1999)

As a result of a four-year long program supported by the National Institute of Dental Research (NIDR), researchers in the electrochemical processing group of MSEL have concluded the development of a mercury-free metallic alternative for conventional dental amalgams.

The use of mercury-containing dental restoratives is restricted severely in Japan and much of Europe. Several alternative materials are in use, but none of them is completely satisfactory. While mercury-containing restoratives are still in use in the United States, there has often been discussion of restricting their use, and it is, therefore, desirable that a better alternative material should be available.

The technology developed in MSEL is based on the ability of silver surfaces to adhere (cold weld) to each other after being treated in dilute fluoboric acid. Silver particles that have been immersed in such acid can be hand-consolidated into cohesive solids (78 percent theoretical density) using conventional dental tools. Over the course of the program, several forms of silver powder were evaluated, and it was determined that the best source of silver was obtained from a two-solution chemical precipitation process (patent pending). The silver powder characteristics required for optimum hand consolidation properties also were determined.

Two of the most important parameters are the agglomerate size and individual particle size of the silver powder. Dramatic increase in both the transverse rupture strength and density of hand consolidated samples was achieved by optimizing the precipitation process and annealing the silver powder. Acid-assisted consolidation (three patents, two issued and one pending), however, was the major finding, which makes silver powder possible as a mercury-free metallic restorative because the acid removes the silver surface oxide and thereby promotes cold welding.

Using the current technology, hand consolidated silver equals or exceeds the transverse rupture strength, shear strength, creep, toughness, corrosion resistance, microleakage, cyclic contact fatigue, and wear properties of conventional amalgam. The results of in vitro biocompatibility testing have shown the mercury-free restorative to equal or exceed the biocompatability of mercury amalgams. Licensing of this technology is available through the Office of Technology Partnerships.

Reference Biomaterial for Orthopedic Research (November 2000)

Reference Material (RM) 8456, an orthopedic grade Ultra High Molecular Weight Polyethylene (UHMWPE), became available in October 2000. RM 8456 is intended primarily for use in mechanical characterization of material properties and laboratory-simulated performance of orthopedic joint replacement implants. The availability of this reference polyethylene is expected to aid in development of improved test methods and materials by providing a benchmark for comparisons. The need for this reference biomaterial was identified at a workshop on reference biomaterials held at NIST and its development was the result of collaboration among a materials supplier, the orthopedic research community, and NIST.

The material used to prepare RM 8456 was donated by Poly Hi Solidur, Inc., MediTECH Division, Fort Wayne, Ind., in a form similar to that from which many orthopedic components are machined: a cylindrical bar with nominal dimensions of 7.62 cm (3 in) in diameter. Reference properties, reported as mean values with their expanded uncertainties, are Young's modulus, tensile yield strength, tensile ultimate strength, and tensile elongation-to-failure. These properties characterize the bar across the center 5.62 cm (2.21 in) of its diameter and down the entire bar length. Material beyond the central 5.62 cm was found to differ significantly from that within.

Magnetic Materials

Magnetization Control (March 2000)

For a large class of magnetic devices, including read heads in hard drives and magnetic random access memory (MRAM) cells, it is important to control the direction of the magnetization in thin films of magnetic metals such as cobalt and Permalloy (Ni80Fe20). Researchers in MSEL's Metallurgy Division have come up with an alternative to the common practice of using antiferromagnetic materials for this purpose. The new method provides an anisotropy (directional magnetization) that is very strong and very homogeneous and that is expected to show high thermal stability. The large anisotropy is found in thin magnetic films deposited on top of obliquely deposited tantalum underlayers. The oblique deposition of the tantalum produces a corrugated tantalum surface as ripples running perpendicular to the atom flux are amplified through shadowing effects. The cobalt, nickel, or iron atoms, deposited at normal incidence, are more mobile than the tantalum atoms, so they fill the 5 nm wide grooves in the tantalum surface and then form a relatively smooth upper surface, resulting in a magnetic film which carries the corrugated imprint of the underlayer.

The low energy states of this structure have the magnetization lying in either direction along the corrugations, parallel to the wavy surface, for the same reason that it easy to magnetize an iron needle parallel to its length: magnetostatic energy is minimized when the magnetization lies parallel to an interface. Thirty nm thick cobalt films have been deposited on corrugated tantalum surface and found to take as much as 0.16 T (1.6 kOe) to rotate the magnetization perpendicular to the corrugations. A second cobalt film, separated from the first cobalt layer by 4 nm of copper, required only 13 mT. The anisotropy generated by the obliquely deposited tantalum underlayers is very uniform, with local anisotropy axis directions varying less than 2 degrees, and anisotropy fields varying by less than 5 mT. Since the anisotropy field is magnetostatic in origin, it is expected to be as thermally stable as the magnetization itself

Pinning Magnetization by a Special Thin-Film Deposition Technique (January 2001)

When materials are deposited onto substrates to make thin films, the usual goal is to produce a smooth deposit. However, recent work in MSEL's Metallurgy Division has shown that rough deposits can have some special advantages. In particular, when the incoming flux of atoms strikes the substrate at an oblique angle, a deposit is formed with a strongly textured surface consisting of parallel ridges and valleys. This structure has some special advantages for the fabrication of magnetic thin-film devices.

In the MSEL work, it was found that a thin layer of tantalum, obliquely deposited, has a textured roughness that can have a strong effect on a magnetic layer deposited on top of it. The textured surface pins the magnetization direction in the magnetic material, producing a magnetic anisotropy. Such pinning of the magnetic direction is needed for the functioning of a special structure known as a spin valve, which is used in modern read heads of computer hard disks. The pinning is strong enough to prevent reversal of the magnetization direction of the magnetic film, and the pinning remains strong at the elevated temperatures that may be encountered during use.

The anisotropy produced by obliquely deposited tantalum thin films has a number of desirable properties: it is strong, it is uniform, and it has good thermal stability. In addition, the system has good corrosion resistance and chemical compatibility. These properties are advantageous, as the increased demand for sensitivity in read heads has led to higher current densities and hotter operating temperatures, and as read heads become smaller to accommodate narrower recorded tracks.

Materials for Microelectronics

Nanocompositional Mapping and Structure Analysis (December 1999)

Barium strontium titanate (BST) is the leading candidate material for the replacement of silicon dioxide dielectrics in the next-generation dynamic random access memory (DRAM) devices. The dielectric properties of BST have been found to be strongly dependent upon composition; the dielectric constant decreases by about 50 percent when the Ti content is increased from 51 percent to 53.5 percent. To understand this strong composition dependence, MSEL researchers have conducted high-resolution electron microscopy and high-spatial resolution electron energy loss spectroscopy measurements to study the microstructure and chemistry of BST films with Ti contents ranging from 50.7 percent to 53.4 percent Ti. The films, obtained from Advanced Technology Materials, Inc., were deposited on Pt/SiO2/Si substrates by metal-organic chemical vapor deposition. The measurements showed that the grain boundaries in all of the films had a higher Ti/Ba ratio than the grain interiors. In addition, films with greater than 52 percent

Ti contained an amorphous Ti-rich phase at some of the grain boundaries and multiple grain junctions. Quantitative spectrum imaging studies have indicated that Ba/Sr cation vacancies segregate to the grain boundary regions. These nanocomposition and structure results are important for understanding the dielectric constant dependence on composition, and for optimizing the deposition process of BST-DRAM films

High Precision Capacitance Cell Developed for Thin Film Out-of-Plane Expansion (February 2000)

Two MSEL Polymers Division researchers, Chad Snyder and Fred Mopsik, have developed a high-precision capacitance cell for measuring the expansion of dielectric, semiconducting, and conducting films between 5 μm and 0.5 cm thick due to changes in temperature and humidity. The new apparatus allows accurate measurements on semiconducting and conducting materials that were not possible with a previous NIST design. The capacitance cell technique is expected to provide researchers in the microelectronics industry with a means of determining the coefficient of thermal expansion of thin film interlevel dielectrics. This metrology was designed to measure films with thicknesses that are between the measurement capabilities of thermomechanical analysis (lower limit of 2 mm) and X-ray reflectivity (upper limit of 0.1 μm).

The previously reported design produced accurate values for the coefficient of thermal expansion of a 0.5 mm thick single crystal <0001> oriented Al2O3 sample. The previous design also was shown to have the ability to measure thin (14 μm) polymer films. Values determined for the thin polymer film were comparable to those obtained by a combination of in-plane expansion measurements and volume dilatometry. The relative expanded uncertainty in the thickness for the previous and current designs is 0.1 × 10-6 while holding isothermally and 1 × 10-6 upon thermal cycling under dry conditions (i.e., 0 percent relative humidity). The limitation of the previous cell was that it was unable to measure conducting or semiconducting samples. Measurements with the previous design on single crystal silicon resulted in damage to the capacitance cell. This damage was due to the creation of a Schottky junction (silicon/nichrome interface) that functioned as a frequency multiplier and took the 1 kHz measurement frequency into the ultrasonic region, thereby breaking the conducting epoxy contacts. The new design electrically isolates the sample using a guard ring on the top and bottom electrodes. The bottom electrode was designed so that its inner electrode diameter was half that of the top to minimize the problems associated with electrode alignment. Measurements on single crystal <100> oriented silicon reproduced recommended literature values within the aforementioned experimental uncertainty. This metrology has a variety of other applications as an extremely sensitive displacement sensor.

Metrology for Development of Embedded Capacitance Technology for High-Speed Electronics (April 2000)

MSEL scientists, in collaboration with industry and academia, are developing test methodology for embedded capacitance technology. There is a widespread need for power-ground decoupling in today's electronic circuits to assure signal integrity and to reduce electromagnetic noise. Currently used discrete capacitors pose several drawbacks, such as the significant manufacturing costs and the amount of surface area they occupy on the electronic assembly. In addition, discrete capacitors do not perform adequately at frequencies above 1 GHz, the frequency regime for today's wireless communication and other high-speed electronics. In looking for a technical solution the National Center for Manufacturing Science, NIST, and more than a dozen industry partners formed a consortium to develop and advance embedded-decoupling-capacitance (EDC) technology. The embedded-decoupling capacitance appears to be the most efficient way to achieve low noise in the voltage driving device, and thus, the highest possible data-speed that otherwise is unobtainable by any other known packaging solution.

Through this multidisciplinary effort over the past two years, the EDC Consortium has identified polymer-ferroelectric- composite materials as one of the primary candidates for this new technology need. The MSEL effort focused on design of test vehicles and procedures for dielectric testing these polymer composite films. Progress on this effort was reviewed at a recent workshop organized by EDC Consortium that attracted over 100 researchers from materials suppliers, circuit manufacturers, original equipment manufacturers, and universities. During the workshop, experts from the consortium members, including NIST, discussed new design guidelines and measurement aspects of the EDC test methodology that led to agreement on further actions towards developing a new standard test procedure for EDC technology.

Testing for Low-Temperature Reliability of HDI Substrates for Motorola (June 2000)

Elizabeth Drexler of MSEL was asked by Motorola to provide low-temperature data on strain and displacements in the microvias of their HDI (high-density interconnect) substrates. Electronic packages are qualified for use in specific environments by passing accelerated lifetime tests. Oneof the more rigorous qualifying tests is thermal cycling between –55 and 125 degrees C for 1,000 or more cycles. Motorola had observed that packages that passed cycling between 0 and 125 degrees C had increased failure rates at this more rigorous temperature span.

This HDI package was complex, containing microvias, blind vias, and solder bumps. It also contained materials with high coefficients of thermal expansion, such as the unfilled build-up layers, solder mask, underfill, and polyimide. Electron-beam moiré was used to measure displacements and calculate strains at various locations on the cross section of the package over a temperature range from –55 to 125 degrees C. Over five thermal cycles, little deformation was observed in the microvias, even though adjacent layers expanded as much as 1.2 percent at 125 degrees C. Additional thermal cycles (34 cycles) were conducted in an environmental chamber. Accumulated deformation in the microvias was negligible; however, cracks developed at the base of the solder bumps and along the sides of the blind vias at several locations.

Electron-beam moiré offers the electronics-packaging industry, perhaps, its only means of measuring deformations at low temperatures and at such a localized scale. This work was supported by OMP, and it will be presented at the upcoming Electronic Component and Technology Conference.

NIST Collaboration Demonstrates Optical Techniques for the Characterization of Polymer Interfaces (June 2000)

Researchers from CSTL (837), PL (844), and MSEL (854) have collaborated on a project developing new procedures based on state-of-the-art femtosecond lasers for the application of vibrationally resolved sum frequency generation (VR-SFG) to the study of the interfaces of thin polymer films.

Polymer thin films have important roles in many industries as varied as semiconductor devices, automobile coatings, and construction materials. The structure at both the free and buried interfaces of thin films are critical to their performance as they can determine characteristics such as adhesion and wear. However, very few analytical techniques have the requisite sensitivity and selectivity to study polymer interfaces.

VR-SFG is a promising tool for the study of interfaces as it is specifically forbidden in the bulk region of centrosymmetric films but allowed at interfaces because of their reduced symmetry. However, when multiple interfaces are present as in the study of thin films, techniques must be developed to distinguish the contributions to the VR-SFG signal from each interface present. Standard practice is to destructively modify the free interface and identify the features that are perturbed. The NIST team developed a general technique, utilizing optical interferences in thin films, to avoid this practice. By systematically varying film thickness, spectra can be acquired that selectively probe the buried or the free interface of the film. Additionally, the NIST approach identifies the experimental conditions that enhance signal levels, allowing for more efficient data acquisition. The approach has been demonstrated in a study of the orientational distribution of the phenyl rings at the interfaces of polystyrene films that have been spin cast onto oxidized Si substrates. At the free interface, the phenyl rings are strongly ordered, with a net orientation directed away from the bulk of the film, into the air. At the buried interface, the level of order is reduced significantly, and the rings have little preference for orientation with respect to the oxidized substrate.

The technique now is being used in studies directly correlating the molecular structure of polymer/polymer interfaces important to electronics applications and reactive polymer blends with their mechanical properties.

NIST-SEMATECH Scientists Unravel the Structure of Nanoporous Thin Films (July 2000)

Collaboration among researchers at SEMATECH and NIST led to development of new metrology to characterize the structure of nanoporous thin film low-k dielectrics for use in next generation integrated circuits. Over the two-year period of collaboration, 25 different types of candidate films have been characterized successfully with results distributed to the member companies of SEMATECH to support efforts in developing low-k dielectrics.

As integrated circuit feature sizes shrink, new low-k dielectric materials are needed to address problems with power consumption, signal propagation delays, and cross-talk between interconnects. One avenue to low-k dielectric materials is the introduction of nanoscale pores into a solid film to lower its effective dielectric constant. However, the pore structure of these low-k dielectrics strongly affects other important material properties, such as mechanical strength, moisture uptake, coefficient of thermal expansion, and adhesion to different substrates. The characterization of the pore structure also is needed to guide development of future low-k materials and processes.

Significant measurement challenges had to be surmounted in the development of metrology to characterize the pore structure of thin nanoporous low-k dielectric films. The small sample volume of 1 m films and the need to characterize the film structure on silicon wafers imposed great challenges to traditional methods for characterizing porous materials. The newly developed NIST-SEMATECH methodology is based on a unique combination of high-resolution X-ray reflectivity and small-angle neutron scattering measurements. Average pore size, film density depth profile, porosity, pore connectivity, moisture uptake, and pore wall density may now be measured. The NIST-SEMATECH methodology is currently the sole measurement technique able to determine the pore wall density directly correlated with mechanical integrity of thin films. The NIST measurement results have facilitated materials and equipment suppliers in the synthesis of a wide range of novel nanoporous films, including many having more complex structures. Work is now in progress to characterize these more complex structures by developing new strategies based upon this methodology. For example, recent developments have enabled characterization of nanoporous films with inhomogeneous wall structures.

Evaluating Ferroelectric Materials for Microwave Electronics (July 2000)

As part of its program on electronic materials, MSEL's Materials Reliability Division has collaborated with the University of Colorado in an investigation of new ferroelectric perovskite oxide thin films for cryogenic and ambient temperature applications. Thin-film ferroelectric materials have received considerable attention because of their growing use in electronic, electro-optic, optical, and acoustic devices. Potential applications include random access memories, pyroelectric detectors, acoustic transducers, and microwave devices. An important characteristic of these materials is the ability to change their dielectric constants by an externally applied electric field (non-linear dielectrics). This idea is being pursued in a class of novel tunable microwave devices such as microstrip line phase shifters, high-Q resonators, and tunable filters. These devices contain both high-temperature-superconducting film and non-linear dielectric film. The former provides low surface resistance and thus intrinsically narrow bandwidths and the latter allows for an easy change in resonant frequency because its dielectric constant is controlled by an external electric field. Of the various non-linear dielectric materials, ferroelectric perovskite oxide-thin films are considered potential candidates for tunable microwave devices because of the high dielectric constant. The team has just released a report on film growth, the structural and low-frequency dielectric properties of the films, and some dielectric data obtained on bulk samples. They also present results on X-ray diffraction studies on some of the films, which clarify the effect of strain on dielectric properties.

MSEL Develops Tool for Understanding Roles of Additives in Superconformal Electrodeposition of Copper (September 2000)

A multidisciplinary effort is under way in MSEL to develop an understanding of superconformal electro-deposition of copper, which recently has been implemented for on chip interconnects. Future demands for high density of interconnects with very short signal delay times require interconnects that are very narrow and have a high electrical conductivity. Superconformal deposition, which is promoted by the presence of small concentrations of additives in the electrolyte, enables the copper to deposit without voids into vias and trenches having high aspect ratios.

Recently MSEL researchers have demonstrated superconformal electrodeposition of copper in 500 nm deep trenches ranging from 500 to 90 nm in width using an acid cupric sulfate electrolyte containing chloride (Cl), polyethylene glycol (PEG), and 3-mercapto-1-propanesulfonate (MPSA). The behavior of the system is representative of several commercial electrolytes and may be employed usefully as a model or "test bed" for exploring the "superfilling" phenomenon. In contrast, similar experiments using either an additive-free electrolyte, or an electrolyte containing the binary combination Cl-PEG, Cl-MPSA, or simply benzotriazole (BTAH), resulted in the formation of a continuous void within the center of the trench. Examination of the current-potential deposition characteristics of the electrolytes reveals an hysteretic response associated with the C1-PEG-MPSA electrolyte that can be employed usefully to monitor and explore additive efficacy and consumption. This provides an easily used tool for developing an understanding of the specific roles of the additives in promoting superfill.

New Texture Measurement Software Now Available on MSEL Web (October 2000)

Many components and devices are fabricated from materials that have a preferred crystallographic orientation or texture. The properties and performance of these components and devices can be highly dependent upon the texture. For example, the remanent polarization in PbZrxTi1-xO3 films used in non-volatile memory devices is orientation-dependent so the ability to switch domains in the devices during a writing operation is strongly influenced by the texture of the film. To optimize the development of textured materials it is desirable to quantify the effects of texture on properties, which requires accurate measurement of the texture. The specialized equipment typically used for texture measurements is not routinely available in most laboratories. MSEL has developed accurate techniques that use commonly available equipment for measuring fiber texture in thin film and bulk materials. The measurement protocol, as well as the TexturePlus software needed to correct and analyze the resulting data, are available on the web at www.ceramics.nist.gov/webbook/TexturePlus/texture.htm. To date, the techniques have been used to measure texture in thin films of Ba1-xSrxTiO3, PbZrxTi1-xO3 and Cu as well as bulk samples of alumina and silicon nitride.

Database on Lead-Free Solders (November 2000)

MSEL’s Materials Reliability Division is working with the Metallurgy Division, the Colorado School of Mines, and the National Electronics Manufacturing Initiative (NEMI) to expand a database on the properties of lead-free solders. With product cycle time being slashed to keep up with consumer demand and competitive pressure, new electronic products are going directly from computer-aided design to full-scale production. The worldwide movement in the electronics industry to replace lead-tin eutectic solders with lead-free solders creates a need for critical data on the industry’s new lead-free solder compositions for these design and reliability models. The team is working with the NEMI Lead-free Alloy Task Group to gather existing physical and mechanical property data that have been developed by researchers around the world into a single database. In addition, the team is working with NEMI to develop a list of missing high-priority data, with the list serving as a roadmap for research in lead-free solders. NIST and NEMI are planning to host a joint national workshop on these issues. The most recent version of the database is posted on the Materials Reliability Website at:
<http://www.boulder.nist.gov/div853/eudora=“autourl”> http://www.boulder.nist.gov/div853/.

Materials for Wireless Communication

Using Processing Conditions to Optimize Material Properties for Dielectrics (December 1999)

Recent progress in microwave telecommunication has necessitated the development of dielectric materials with stringent specifications: the largest possible dielectric constant, the lowest dielectric loss, and near-zero temperature coefficient of the dielectric constant. Most of the best materials are based on complex perovskite oxides. Such materials often have an elaborate microstructure of domains and interfaces. The dielectric properties of these materials are sensitive to the structural and micro-structural features and, therefore, the understanding of the properties/structure interrelation is paramount in further development of these materials. A joint effort between MSEL's Metallurgy and Ceramics Divisions and the NIST Center for Neutron Research is working toward a resolution of some of these issues.

Transmission electron microscopy (TEM) is extremely well suited for study of complex perovskite oxides because of the great sensitivity of electron scattering to structural features such as ordering, and for the technique's ability to image domains and interfaces. The researchers' recent TEM studies have resulted in complete characterization of several complex systems, including layered structures of Srn(Nb,Ti)nO3n+2 and ordered Ca(Ca,Nb,Ti)O3. The Ca(Ca,Nb,Ti)O3 system was found to be very rich with respect to different types of ordering. This system, which had not been studied by other research groups, offers a rich variety of order/microstructure states and, thus, opportunities to change the dielectric properties. These states can be well controlled and are expected to have a significant effect on the dielectric properties of interest.

For the TEM study, phase diagrams and structural models of unknown compounds were developed. Neutron and ray diffraction results helped refine the structural models. Changes in the temperature coefficient of the dielectric constant from positive to negative were identified and related to the structural details. As a direct result of this work, the researchers were able to explain, for the $Ca_5Nb_2TiO_{12}$ composition patented by Lucent Technologies, how the dramatic effect of sintering temperature on the dielectric constant and its temperature coefficient could be attributed to changes in the type of ordering and microdomain state of the material. This type of information serves as a guide to using processing conditions to optimize material properties.

Computational Studies Advance Atomistic Understanding of Electronic Ceramics (April 2000)

Recent computational studies by MSEL Ceramics Division researchers have made significant advances in elucidating the microscopic origins of the behaviors of two types of electronic ceramics. The first type, lead-containing perovskite ceramics, $PbB_{1/3}B'_{2/3}O_3$ (B and B' are metal ions such as Mg^{2+}, Ti^{4+}, and Nb^{5+}), are currently used in actuators and sonar/medical imaging transducers. The electrical properties of these materials are sensitive functions of the precise arrangements of the metal ions in the crystal structure; hence, carefully controlled processing is required to achieve optimized properties. First-principles total energy calculations have revealed a complex many-body interaction between lead and certain oxygens that explains atomistically why the B cations disorder at much lower temperatures when the ceramics contain Pb instead of Ba. Typically, Pb-O bonds are stronger and more covalent than Ba-O bonds because Pb has a lone-pair of 6sp electrons—this type of interaction results in technically important properties such as ferroelectricity in $PbTiO_3$. The computational results showed that this Pb-O interaction is further enhanced when the oxygen is “underbonded”; i.e., when the other cations bonded to that oxygen are relatively low in charge. For example, the oxygen in a Mg^{2+}-O-Mg^{2+} environment is underbonded and reacts more strongly with Pb than an oxygen in a Ti^{4+}-O-Ti^{4+} environment. These results explain why, how, and under what conditions metal ions order and/or disorder, and are immediately useful for property optimization.

The second electronic ceramic, $CaTiO_3$, is used in base station filters and resonators for wireless communications. The dielectric constant of $CaTiO_3$ is nearly 200, which is unusually high for a non-ferroelectric material. First-principles calculations reveal the microscopic origin of these unusual electrical properties. Computed phonon spectra and dielectric constant indicated that interatomic forces in $CaTiO_3$ are characterized by a delicate balance between electrostatic attraction and short-range repulsion, which results in a set of low-frequency phonons that have large amplitudes in an applied electric field—these phonons are the direct cause of the high dielectric constant. The results also revealed the nature of these critical phonons as modes in which the Ca^{2+} and Ti^{4+} cations move together in a direction opposite that of the negatively charged oxygens—this explains chemically why the polarization associated with these modes is maximized, and the very high dielectric constant is observed. These results provide fundamental knowledge useful for the rational design and prediction of materials with controlled properties.

OTHER

Transmittal Page of U.S. Constitution Sealed in New Encasement (April 2000)

Resulting from the outstanding effort by a large number of NIST staff from CSTL, MSEL, PL, and MEL, the transmittal page of the U.S. Constitution has been sealed in the first of the new encasements for the Charters of Freedom documents (i.e., Constitution, Declaration of Independence, and Bill of Rights). Michael McGlauflin, Eric Whitenton, and guest worker Charles Tilford of MEL's Automated Production Technology Division were present on Feb. 23 to close the valves to complete the gas filling and sealing of the first encasement. The encasement is filled with humidified argon (40 percent relative humidity at the display temperature) with parts-per-million-level residual oxygen. This accomplishment represents the end of the beginning for the project team. Next, the project team must build the second "prototype" (of a smaller size) and then complete the production run of seven more encasements. The final drawings for the remaining eight encasements are nearing completion and actual fabrication will start before the end of March 2000. The ability to draw on the diverse expertise of so many NIST staff has enabled this project to meet the extremely challenging performance and schedules demanded by the National Archives and Records Administration.